

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
17 March 2005 (17.03.2005)

PCT

(10) International Publication Number  
WO 2005/023890 A1

(51) International Patent Classification<sup>7</sup>: C08F 297/08, (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number:  
PCT/EP2004/008761

(22) International Filing Date: 4 August 2004 (04.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
03102735.2 11 September 2003 (11.09.2003) EP  
60/503,283 16 September 2003 (16.09.2003) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

## Declaration under Rule 4.17:

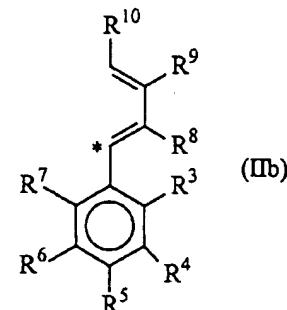
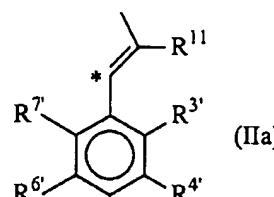
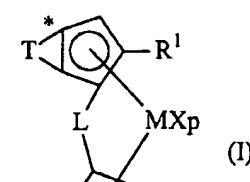
— of inventorship (Rule 4.17(iv)) for US only

## Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MULTISTEP PROCESS FOR PREPARING HETEROPHASIC PROPYLENE COPOLYMERS



(57) Abstract: A multistage process comprising the step of polymerizing propylene in the presence of a catalysts system, comprising one or more metallocene compound of formula (I): wherein M is an atom of a transition metal; p is an integer from 0 to 3, X, same or different, is a hydrogen atom, a halogen atom, or a hydrocarbon group; L is a divalent bridging R<sup>1</sup> and R<sup>2</sup>, are C<sub>1</sub>-C<sub>20</sub>-alkyl radicals; T, equal to or different from each other, is a moiety of formula (IIb) or (IIa): wherein R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup> are hydrogen atoms or hydrocarbon groups; with the proviso that at least one among R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> is different from hydrogen; R<sup>11</sup> is a hydrogen atom or a hydrocarbon group; R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup>, are hydrogen atoms or hydrocarbon groups; and further comprising the step of contacting, under polymerization conditions, in a gas phase, ethylene and one or more comonomers. Where the amount of the polymer obtained in the first step ranges from 4% by weight and 20% by weight, extremes excluded, of the polymer obtained in the whole process.

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## MULTISTEP PROCESS FOR PREPARING HETEROPHASIC PROPYLENE COPOLYMERS

The present invention relates to a multistep process for preparing heterophasic propylene copolymers, by using a metallocene-based catalyst.

Multistep processes for the polymerization of olefins, carried out in two or more reactors, are known from the patent literature and are of particular interest in industrial practice. The possibility of independently varying, in any reactors, process parameters such as temperature, pressure, type and concentration of monomers, concentration of hydrogen or other molecular weight regulator, provides much greater flexibility in controlling the composition and properties of the end product compared to single-step processes. Multistep processes are generally carried out using the same catalyst in the various steps/reactors. The product obtained in one reactor is discharged and sent directly to the next step/reactor without altering the nature of the catalyst.

Usually a crystalline polymer is prepared in the first stage followed by a second stage in which an elastomeric copolymer is obtained. The monomer used in the first stage is usually also used as comonomer in the second stage. This simplifies the process, for the reason that it is not necessary to remove the unreacted monomer from the first stage, but this kind of process has the drawback that only a limited range of products can be prepared.

One of the aim of these processes is to prepare "soft" polymers in which the elastomeric polymer grows on a crystalline matrix. In order to make the final polymer as soft as possible it is desirable to have a large amount of elastomer on the crystalline matrix. The threshold content of elastomer is related to the stickiness of the final polymer: if the resulting heterophasic polymer is sticky, the particles agglomerate and adhere to the walls of the reactor, thus rendering an industrial production impossible.

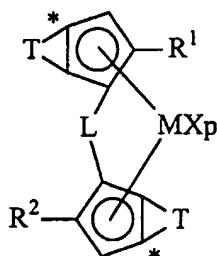
US 5,854,354 discloses a multistep process in which a propylene polymer is prepared in step a) followed by an ethylene (co)polymer prepared in step b). This document describes that the amount of the ethylene polymer ranges from 20% to 80% by weight of the total polymer, but in the examples only compositions containing about 30% of ethylene polymer are prepared.

Thus it should be desirable to find a multistage process that permits to obtain a heterophasic polymer containing a large amount of elastomer and limiting at the same time the stickiness of the final polymer.

An object of the present invention is a multistage process carried out by using a particular class of metallocene compounds in which in the second stage the amount of ethylene copolymers prepared is higher than 80% of the total polymer obtained.

The multistage process according to the present invention comprises the following steps:

- a) polymerizing propylene and optionally one or more monomers selected from ethylene and alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ , wherein  $\text{T}^1$  is a  $\text{C}_2\text{-C}_{20}$  alkyl radical in the presence of a catalysts system, supported on an inert carrier comprising:
- i) one or more metallocene compound of formula (I):



(I)

wherein:

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements; preferably M is titanium, zirconium or hafnium;

p is an integer from 0 to 3, preferably p is 2, being equal to the formal oxidation state of the metal M minus 2;

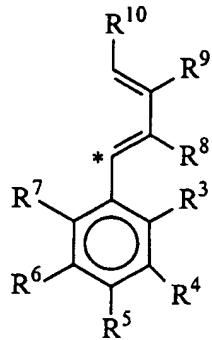
X, same or different, is a hydrogen atom, a halogen atom, or a R, OR,  $\text{OSO}_2\text{CF}_3$ , OCOR, SR, NR<sub>2</sub> or PR<sub>2</sub> group, wherein R is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_3\text{-C}_{20}$  cycloalkyl,  $\text{C}_6\text{-C}_{20}$  aryl,  $\text{C}_7\text{-C}_{20}$  alkylaryl or  $\text{C}_7\text{-C}_{20}$  arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR'O group wherein R' is a divalent radical selected from  $\text{C}_1\text{-C}_{20}$  alkylidene,  $\text{C}_6\text{-C}_{40}$  arylidene,  $\text{C}_7\text{-C}_{40}$  alkylarylidene and  $\text{C}_7\text{-C}_{40}$  arylalkylidene radicals; preferably X is a hydrogen atom, a halogen atom or a R group; more preferably X is chlorine or a methyl radical;

L is a divalent bridging group selected from  $\text{C}_1\text{-C}_{20}$  alkylidene,  $\text{C}_3\text{-C}_{20}$  cycloalkylidene,  $\text{C}_6\text{-C}_{20}$  arylidene,  $\text{C}_7\text{-C}_{20}$  alkylarylidene, or  $\text{C}_7\text{-C}_{20}$  arylalkylidene radicals optionally

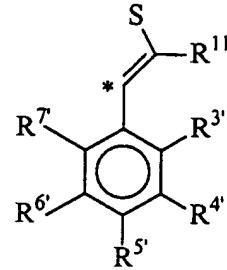
containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms such as  $\text{SiMe}_2$ ,  $\text{SiPh}_2$ ; preferably L is selected from the group consisting of is  $\text{Si}(\text{CH}_3)_2$ ,  $\text{SiPh}_2$ ,  $\text{SiPhMe}$ ,  $\text{SiMe}(\text{SiMe}_3)$ ,  $\text{CH}_2$ ,  $(\text{CH}_2)_2$ ,  $(\text{CH}_2)_3$  and  $\text{C}(\text{CH}_3)_2$ ;

$\text{R}^1$  and  $\text{R}^2$ , equal to or different from each other, are linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $\text{R}^1$  and  $\text{R}^2$  are methyl, ethyl or isopropyl radicals, with the proviso that at least one of  $\text{R}^1$  and  $\text{R}^2$  is not branched;

T, equal to or different from each other, is a moiety of formula (IIa) or (IIb):



(IIa)



(IIb)

wherein:

the atom marked with the symbol \* bonds the atom marked with the same symbol in the compound of formula (I);

$\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$ , equal to or different from each other, are hydrogen atoms or linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{40}$ -alkyl,  $\text{C}_3\text{-C}_{40}$ -cycloalkyl,  $\text{C}_6\text{-C}_{40}$ -aryl,  $\text{C}_7\text{-C}_{40}$ -alkylaryl, or  $\text{C}_7\text{-C}_{40}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear  $\text{C}_1\text{-C}_{20}$  alkyl substituents; with the proviso that at least one among  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$ ,  $\text{R}^6$  and  $\text{R}^7$  is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{40}$ -alkyl,  $\text{C}_3\text{-C}_{40}$ -cycloalkyl,  $\text{C}_6\text{-C}_{40}$ -aryl,  $\text{C}_7\text{-C}_{40}$ -alkylaryl, or  $\text{C}_7\text{-C}_{40}$ -arylalkyl radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

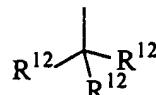
$\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$ , equal to or different from each other, are hydrogen atoms or linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$ -alkyl,  $\text{C}_3\text{-C}_{20}$ -cycloalkyl,  $\text{C}_6\text{-C}_{20}$ -aryl,

$C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $R^8$ ,  $R^9$  and  $R^{10}$  can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear one or more  $C_1$ - $C_{10}$  alkyl substituents;

$R^{11}$  is a hydrogen atom or a linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably  $R^{11}$  is a linear or branched, saturated  $C_1$ - $C_{20}$ -alkyl, such as a methyl, ethyl or isopropyl radical;

$R^{3'}$ ,  $R^{4'}$ ,  $R^{5'}$ ,  $R^{6'}$  and  $R^{7'}$  equal to or different from each other, are hydrogen atoms or linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $R^{3'}$ ,  $R^{4'}$ ,  $R^{5'}$ ,  $R^{6'}$  and  $R^{7'}$  can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear  $C_1$ - $C_{10}$  alkyl substituents;

preferably at least one among  $R^{3'}$ ,  $R^{4'}$ ,  $R^{5'}$ ,  $R^{6'}$  and  $R^{7'}$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably at least one among  $R^{3'}$ ,  $R^{4'}$ ,  $R^{5'}$ ,  $R^{6'}$  and  $R^{7'}$  is a branched  $C_1$ - $C_{40}$ -alkyl radical, more preferably at least one among  $R^{3'}$ ,  $R^{4'}$ ,  $R^{5'}$ ,  $R^{6'}$  and  $R^{7'}$  is a group of formula (III):



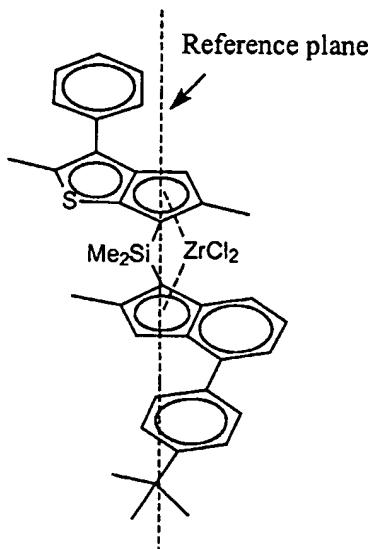
(III)

wherein  $R^{12}$ , equal to or different from each other, is a  $C_1$ - $C_{10}$  alkyl radical, preferably  $R^{12}$  is a methyl or ethyl radical;

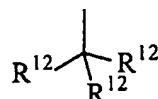
- ii) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally
- iii) an organo aluminum compound;
- b) contacting, under polymerization conditions, in a gas phase, ethylene with one or more alpha olefins of formula  $CH_2=CHT^1$ , wherein  $T^1$  is a  $C_2$ - $C_{20}$  alkyl radical, and optionally with a non-conjugated diene, in the presence of the polymer obtained in step a) and optionally in the presence of an additional organo aluminum compound;

wherein the amount of the polymer obtained in step a) is higher than 4% and lower than 20% by weight of the polymer obtained in the whole process and the amount of polymer obtained in step b) is higher than 80% by weight and lower than 96% by weight of the polymer obtained in the whole process.

The compound of formula (I) is preferably in the form of the racemic or racemic-like isomer. "Racemic-like" means that the benzo or thiophene moieties of the two  $\pi$ -ligands on the metallocene compound of formula (I) are on the opposite sides with respect to the plane containing the central metal atom M and the centre of the cyclopentadienyl moieties as shown in the following compound.



Preferably in the compound of formula (I)  $R^5$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably  $R^5$  is a branched  $C_1$ - $C_{40}$ -alkyl radical, more preferably  $R^5$  is a group of formula (III):



(III)

wherein  $R^{12}$ , equal to or different from each other, is a  $C_1$ - $C_{10}$  alkyl radical, preferably  $R^{12}$  is a methyl or ethyl radical;

Preferably  $R^5$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radical, optionally

containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably  $R^5$  is a branched  $C_1$ - $C_{40}$ -alkyl radical, more preferably  $R^5$  is a group of formula (III) described above.

Preferably in the compounds of formula (IIa)  $R^3$ ,  $R^4$ ,  $R^6$  and  $R^7$ , are hydrogen atoms.

Preferably in the compounds of formula (IIb)  $R^3$ ,  $R^4$ ,  $R^6$  and  $R^7$  are hydrogen atoms.

In an embodiment, in the compound of formula (I) T are the same and they have formula (IIa) wherein  $R^9$  is a  $C_1$ - $C_{20}$  alkyl radical; preferably it is a  $C_1$ - $C_{10}$  alkyl radical; more preferably  $R^9$  is a methyl or ethyl group.

In a further embodiment, in the compound of formula (I) T are the same and they have formula (IIb).

In a further embodiment, in the compound of formula (I) T are the same and they have formula (IIa) wherein  $R^9$  is hydrogen atom.

In a further embodiment, in the compound of formula (I) T are different and they have formulas (IIb) and (IIa).

In a still further embodiment, in the compound of formula (I) T are the same and they have formula (IIb) wherein  $R^{11}$  is a linear or branched, saturated  $C_1$ - $C_{20}$ -alkyl radical, such as a methyl, ethyl or isopropyl radical.

Compounds of formula (I) are known in the art, for example they can be prepared according to according to WO 98/40331, WO 01/48034, PCT/EP02/13552 and DE 10324541.3.

The catalyst system used in the process of the present invention is supported on an inert carrier. This is achieved by depositing the metallocene compound i) or the product of the reaction thereof with the component ii), or the component ii) and then the metallocene compound i) on an inert support. Examples of inert supports are inorganic oxides such as, for example, silica, alumina, Al-Si, Al-Mg mixed oxides, magnesium halides, organic polymeric supports such as styrene/divinylbenzene copolymers, polyethylene or polypropylene. The supportation process is carried out in an inert solvent, such as hydrocarbon selected from toluene, hexane, pentane and propane and at a temperature ranging from 0°C to 100°C, more preferably from 30°C to 60°C.

Preferred supports are porous organic polymers such as styrene/divinylbenzene copolymers, polyamides, or polyolefins.

Preferably porous alpha-olefin polymers are polyethylene, polypropylene, polybutene, copolymers of propylene and copolymers of ethylene.

Two particularly suitable classes of porous propylene polymers are those obtained according to WO 01/46272 and WO 02/051887 particularly good results are obtained when the catalyst described WO 01/46272 is used with the process described in WO 02/051887. Polymers obtained according to WO 01/46272 have a high content of the so-called stereoblocks, i.e. of polymer fractions which, although predominantly isotactic, contain a not negligible amount of non-isotactic sequences of propylene units. In the conventional fractionation techniques such as the TREF (Temperature Rising Elution Temperature) those fractions are eluted at temperatures lower than those necessary for the more isotactic fractions. The polymers obtained according to the process described in WO 02/051887 show improved porosity.

The porous organic polymer has preferably porosity due to pores with diameter up 10  $\mu\text{m}$  (100000 Å) measured to the method reported below, higher than 0.1 cc/g preferably comprised between 0.2 cc/g to 2 cc/g; more preferably from 0.3 cc/g to 1 cc/g.

In the porous organic polymer fit as support according to the process of the present invention, the total porosity due to all pores whose diameter is comprised between 0.1  $\mu\text{m}$  (1000 Å) and 2  $\mu\text{m}$  (20000 Å) is at least 30% of the total porosity due to all pores whose diameter is comprised between 0.02  $\mu\text{m}$  (200 Å) and 10  $\mu\text{m}$  (100000 Å). Preferably the total porosity due to all pores whose diameter is comprised between 0.1  $\mu\text{m}$  (1000 Å) and 2  $\mu\text{m}$  (20000 Å) is at least 40% of the total porosity due to all pores whose diameter is comprised between 0.02  $\mu\text{m}$  (200 Å) and 10  $\mu\text{m}$  (100000 Å). More preferably the total porosity due all pores whose diameter is comprised between 0.1  $\mu\text{m}$  (1000 Å) and 2  $\mu\text{m}$  (20000 Å) is at least 50% of the total porosity due all pores whose diameter is comprised between 0.02  $\mu\text{m}$  (200 Å) and 10  $\mu\text{m}$  (100000 Å).

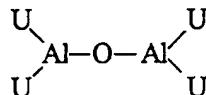
A particularly suitable process for supporting the catalyst system is described in WO 01/44319, wherein the process comprises the steps of:

- (a) preparing a catalyst solution comprising a catalyst system;
- (b) introducing into a contacting vessel:
  - (i) a porous support material in particle form, and
  - (ii) a volume of the catalyst solution not greater than the total pore volume of the porous support material introduced;
- (c) discharging the material resulting from step (b) from the contacting vessel and suspending it in an inert gas flow, under such conditions that the solvent evaporates; and

reintroducing at least part of the material resulting from step (c) into the contacting vessel together with another volume of the catalyst solution not greater than the total pore volume of the reintroduced material.

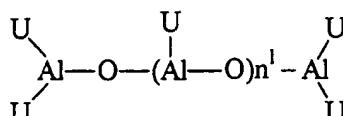
Alumoxanes used as component ii) can be obtained by reacting water with an organo-aluminium compound of formula  $H_jAlU_{3-j}$  or  $H_jAl_2U_{6-j}$ , where U substituents, same or different, are hydrogen atoms, halogen atoms, C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cyclalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radical, optionally containing silicon or germanium atoms with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and 100:1. The molar ratio between aluminium and the metal of the metallocene generally is comprised between about 10:1 and about 20000:1, and more preferably between about 100:1 and about 5000:1.

The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

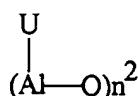


wherein the substituents U, same or different, are defined above.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n<sup>1</sup> is 0 or an integer of from 1 to 40 and the substituents U are defined as above; or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n<sup>2</sup> is an integer from 2 to 40 and the U substituents are defined as above.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO).

Particularly interesting cocatalysts are those described in WO 99/21899 and in WO01/21674 in which the alkyl and aryl groups have specific branched patterns. Non-limiting examples of aluminium compounds that can be reacted with water to give suitable alumoxanes (b), described in WO 99/21899 and WO01/21674, are:

tris(2,3,3-trimethyl-butyl)aluminium, tris(2,3-dimethyl-hexyl)aluminium,  
tris(2,3-dimethyl-butyl)aluminium, tris(2,3-dimethyl-pentyl)aluminium,  
tris(2,3-dimethyl-heptyl)aluminium, tris(2-methyl-3-ethyl-pentyl)aluminium,  
tris(2-methyl-3-ethyl-hexyl)aluminium, tris(2-methyl-3-ethyl-heptyl)aluminium,  
tris(2-methyl-3-propyl-hexyl)aluminium, tris(2-ethyl-3-methyl-butyl)aluminium,  
tris(2-ethyl-3-methyl-pentyl)aluminium, tris(2,3-diethyl-pentyl)aluminium,  
tris(2-propyl-3-methyl-butyl)aluminium, tris(2-isopropyl-3-methyl-  
butyl)aluminium, tris(2-isobutyl-3-methyl-pentyl)aluminium, tris(2,3,3-trimethyl-  
pentyl)aluminium, tris(2,3,3-trimethyl-hexyl)aluminium, tris(2-ethyl-3,3-dimethyl-  
butyl)aluminium, tris(2-ethyl-3,3-dimethyl-pentyl)aluminium, tris(2-isopropyl-3,3-  
dimethyl-butyl)aluminium, tris(2-trimethylsilyl-propyl)aluminium, tris(2-methyl-3-  
phenyl-butyl)aluminium, tris(2-ethyl-3-phenyl-butyl)aluminium, tris(2,3-dimethyl-  
3-phenyl-butyl)aluminium, tris(2-phenyl-propyl)aluminium, tris[2-(4-fluoro-  
phenyl)-propyl]aluminium, tris[2-(4-chloro-phenyl)-propyl]aluminium, tris[2-(3-  
isopropyl-phenyl)-propyl]aluminium, tris(2-phenyl-butyl)aluminium,  
tris(3-methyl-2-phenyl-butyl)aluminium, tris(2-phenyl-pentyl)aluminium, tris[2-  
(pentafluorophenyl)-propyl]aluminium, tris[2,2-diphenyl-ethyl]aluminium and  
tris[2-phenyl-2-methyl-propyl]aluminium, as well as the corresponding  
compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen  
atom, and those wherein one or two of the hydrocarbyl groups are replaced with an  
isobutyl group.

Amongst the above aluminium compounds, trimethylaluminium (TMA),  
triisobutylaluminium (TIBA), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA),  
tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-  
trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are  
compounds of formula  $D^+E^-$ , wherein  $D^+$  is a Brønsted acid, able to donate a proton  
and to react irreversibly with a substituent X of the metallocene of formula (I) and  
 $E^-$  is a compatible anion, which is able to stabilize the active catalytic species

originating from the reaction of the two compounds, and which is sufficiently labile to be removed by an olefinic monomer. Preferably, the anion E<sup>-</sup> comprises one or more boron atoms. More preferably, the anion E<sup>-</sup> is an anion of the formula BAr<sub>4</sub><sup>(-)</sup>, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred compound, as described in WO 91/02012. Moreover, compounds of formula BAr<sub>3</sub> can be conveniently used. Compounds of this type are described, for example, in the International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula BAr<sub>3</sub>P wherein P is a substituted or unsubstituted pyrrol radical. These compounds are described in WO01/62764. Compounds containing boron atoms can be conveniently supported according to the description of DE-A-19962814 and DE-A-19962910. All these compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2:1; more preferably about 1:1.

Non limiting examples of compounds of formula D<sup>+</sup>E<sup>-</sup> are:

Triethylammoniumtetra(phenyl)borate,  
Tributylammoniumtetra(phenyl)borate,  
Trimethylammoniumtetra(tolyl)borate,  
Tributylammoniumtetra(tolyl)borate,  
Tributylammoniumtetra(pentafluorophenyl)borate,  
Tributylammoniumtetra(pentafluorophenyl)aluminate,  
Tripropylammoniumtetra(dimethylphenyl)borate,  
Tributylammoniumtetra(trifluoromethylphenyl)borate,  
Tributylammoniumtetra(4-fluorophenyl)borate,  
N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,  
N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,  
N,N-Dimethylaniliniumtetra(phenyl)borate,  
N,N-Diethylaniliniumtetra(phenyl)borate,  
N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,  
N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,  
N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,

N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,  
Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,  
Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,  
Triphenylphosphoniumtetrakis(phenyl)borate,  
Triethylphosphoniumtetrakis(phenyl)borate,  
Diphenylphosphoniumtetrakis(phenyl)borate,  
Tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,  
Tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,  
Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,  
Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,  
Triphenylcarbeniumtetrakis(phenyl)aluminate,  
Ferroceniumtetrakis(pentafluorophenyl)borate,  
Ferroceniumtetrakis(pentafluorophenyl)aluminate.  
Triphenylcarbeniumtetrakis(pentafluorophenyl)borate, and  
N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate.

Organic aluminum compounds used as compound iii) are those of formula  $H_jAlU_{3-j}$  or  $H_jAl_2U_{6-j}$  as described above.

Preferably step a) further comprises a prepolymerization step a-1).

The prepolymerization step a-1) can be carried out by contacting the catalyst system with ethylene and/or propylene and/or one or more alpha olefins of formula  $CH_2=CHT^1$ , wherein  $T^1$  is a  $C_2-C_{20}$  alkyl radical; preferably propylene or ethylene are used. The prepolymerization temperature ranges from -20°C to 70°C, in order to obtain a prepolymerized catalyst system preferably containing from 5 to 500 g of polymer per gram of catalyst system.

Thus preferably step a) comprises

- a-1) contacting the catalyst system described above with ethylene and/or propylene and/or one or more alpha olefins of formula  $CH_2=CHT^1$ , wherein  $T^1$  is a  $C_2-C_{20}$  alkyl radical; preferably propylene or ethylene, in order to obtain a prepolymerized catalyst system preferably containing from 5 to 500 g of polymer per gram of catalyst system;
- a-2) polymerizing propylene and optionally one or more monomers selected from ethylene and alpha olefins of formula  $CH_2=CHT^1$ , wherein  $T^1$  is a  $C_2-C_{20}$  alkyl radical in the presence of the prepolymerized catalyst system obtained in step a-1).

Step a) of the present invention can be carried out in liquid phase, in which the polymerization medium can be an inert hydrocarbon solvent or the polymerization medium can be liquid propylene optionally in the presence of an inert hydrocarbon solvent, and of ethylene or one or more comonomer of formula  $\text{CH}_2=\text{CHT}^1$ , or step a) can be carried out in a gas phase. Said hydrocarbon solvent can be either aromatic (such as toluene) or aliphatic (such as propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane).

Preferably the polymerization medium is liquid propylene. It can optionally contains minor amounts (up to 20% by weight, preferably up to 10% by weight, more preferably up to 5% by weight) of an inert hydrocarbon solvent or of one or more comonomer such as ethylene or alpha-olefins of formula  $\text{CH}_2=\text{CHT}^1$ .

Step a) can be carried out in the presence of hydrogen. The amount of hydrogen present during the polymerization reaction is preferably more than 1 ppm; more preferably from 5 to 2000 ppm; even more preferably from 6 to 500 ppm with respect to the propylene present in the reactor. Hydrogen can be added either at the beginning of the polymerization reaction or it can also be added at a later stage after a prepolymerization step has been carried out.

The propylene polymer obtained in step a) is a propylene homopolymer or a propylene copolymer containing up to 20% by mol preferably from 0.1 to 10% by mol, more preferably from 1% to 5% by mol of derived units of ethylene or one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ . Non-limiting examples of alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$  which can be used in the process of the invention are 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred comonomers are ethylene or 1-butene.

The amount of polymer obtained in step a) is higher than 4% by weight and lower than 20% by weight of the total polymer produced in the whole process, preferably it ranges from 10% to 18% by weight of the total polymer produced in the whole process.

preferably in step a) a propylene homopolymer is prepared.

Step b) is carried out in a gas phase, preferably in a fluidized bed reactor or in a continuos stirrer tank reactor. The polymerization temperature is generally comprised between -100°C and +200°C, and, suitably, between 10°C and +90°C. The polymerization pressure is generally comprised between 0,5 and 100 bar. The amount of polymer obtained in step

b) is higher than 80% by weight and lower than 94% by weight of the polymer produced in the whole process, preferably it ranges from 82% to 90% by weight.

Step b) can be carried out in the presence of hydrogen. The amount of hydrogen present during the polymerization reaction is preferably more than 1 ppm with respect to the ethylene present in the reactor; more preferably from 5 to 2000 ppm; even more preferably from 6 to 500 ppm.

In step b) an ethylene copolymer having from 3% by mol to 60% by mol, preferably from 5% by mol to 45% by mol of derived units of comonomers of formula  $\text{CH}_2=\text{CHT}^1$  and optionally up to 20% of derived units of non conjugated diene, is produced. Examples of comonomer of formula  $\text{CH}_2=\text{CHT}^1$  that can be used in step b) of the present invention are: 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 4,6-dimethyl-1-heptene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Preferred comonomer is 1-butene.

The polymer obtained in step b) can optionally contain up to 20% by mol of a non conjugated diene. Non conjugated dienes can be a straight chain, branched chain or cyclic hydrocarbon diene having from 6 to 20 carbon atoms. Examples of suitable non-conjugated dienes are:

- straight chain acyclic dienes, such as 1,4-hexadiene and 1,6-octadiene;
- branched chain acyclic dienes, such as 5-methyl-1,4-hexadiene, 3,7-dimethyl-1,6-octadiene, 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydro myricene and dihydroocinene;
- single ring alicyclic dienes, such as 1,3-cyclopentadiene, 1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,5-cyclododecadiene;
- multi-ring alicyclic fused and bridged ring dienes, such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2, 5-diene; and
- alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes, such as 5-methylene-2-norbornene (MNB), 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene and norbornadiene.

Preferred dienes are 1,4-hexadiene (HD), 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-norbornene (MNB) and dicyclopentadiene (DCPD).

Particularly preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD).

When present the non-conjugated dienes are generally incorporated into the polymer in an amount from 0.1% to about 20% by mol; preferably from 1% to 15% by mol, and more preferably from 2% to 7% by mol. If desired, more than one diene may be incorporated simultaneously, for example HD and ENB, with total diene incorporation within the limits specified above.

The process of the present invention can be carried out in one reactor or in two or more reactor in series.

The following examples are given to illustrate and not to limit the invention.

### Examples

#### General characterization

##### Determination of X.S.

2.5g of polymer were dissolved in 250 ml of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer (X.S.) and then, by difference, the insolubles (X.I.).

##### NMR

The proton and carbon spectra of polymers were obtained using a Bruker DPX 400 spectrometer operating in the Fourier transform mode at 120°C at 400.13 MHz and 100.61 MHz respectively. The samples were dissolved in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. As reference the residual peak of C<sub>2</sub>DHCl<sub>4</sub> in the <sup>1</sup>H spectra (5.95 ppm) and the peak of the *mmmm* pentad in the <sup>13</sup>C spectra (21.8 ppm) were used. Proton spectra were acquired with a 45° pulse and 5 seconds of delay between pulses; 256 transients were stored for each spectrum. The carbon spectra were acquired with a 90° pulse and 12 seconds (15 seconds for ethylene based polymers) of delay between pulses and CPD (waltz 16) to remove <sup>1</sup>H-<sup>13</sup>C couplings. About 3000 transients were stored for each spectrum.

The intrinsic viscosity (I.V.) was measured in tetrahydronaphthalene (THN) at 135°C.

##### Porosity (mercury)

It is determined by immersing a known quantity of the sample in a known quantity of mercury inside a dilatometer and gradually hydraulically increasing the pressure of the mercury. The pressure of introduction of the mercury in the pores is in function of the diameter of the same. The measurement was carried out using a porosimeter "Porosimeter 2000 Series" (Carlo Erba). The total

porosity was calculated from the volume decrease of the mercury and the values of the pressure applied.

The porosity expressed as percentage of voids (%V/V<sub>1</sub>) is determined by absorption of mercury under pressure. The volume of mercury absorbed corresponds to the volume of the pores. For this determination, a calibrated dilatometer (diameter 3 mm) CD3 (Carlo Erba) connected to a reservoir of mercury and to a high-vacuum pump (1x10<sup>-2</sup> mbar) is used. A weighed amount of sample (about 0,5 g) is placed in the dilatometer. The apparatus is then placed under high vacuum (<0,1 mm Hg) and is maintained in these conditions for 10 minutes. The dilatometer is then connected to the mercury reservoir and the mercury is allowed to flow slowly into it until it reaches the level marked on the dilatometer at a height of 10 cm. The valve that connects the dilatometer to the vacuum pump is closed and the apparatus is pressurized with nitrogen (2,5 Kg/cm<sup>2</sup>). Under the effect of the pressure, the mercury penetrates into the pores and the level goes down according to the porosity of the material. Once the level at which the mercury has stabilized has been measured on the dilatometer, the volume of the pores is calculated from the equation  $V = R^2\pi\Delta H$ , where R is the radius of the dilatometer and  $\Delta H$  is the difference in cm between the initial and the final levels of the mercury in the dilatometer. By weighting the dilatometer, dilatometer+mercury, dilatometer+mercury+sample, the value of the apparent volume V<sub>1</sub> of the sample prior to penetration of the pores can be calculated. The volume of the sample is given by:

$$V_1 = [P_1 - (P_2 - P)]/D$$

P is the weight of the sample in grams, P<sub>1</sub> is the weight of the dilatometer+mercury in grams, P<sub>2</sub> is the weight of the dilatometer+mercury+sample in grams, D is the density of mercury (at 25°C = 13,546 g/cc). The percentage porosity is given by the relation:

$$X = (100V)/V_1.$$

The pore distribution curve, and the average pore size are directly calculated from the integral pore distribution curve which is function of the volume reduction of the mercury and applied pressure values (all these data are provided and elaborated by the porosimeter associated computer which is equipped with a "MILESTONE 200/2.04" program by C. Erba.

Bulk density (PBD) was measured according to DIN-53194.

#### **Metallocene compounds**

*rac*-dimethylsilylbis(2-methyl-4-(*para*-tert-butylphenyl)-indenyl)-zirconium dichloride (*rac*-Me<sub>2</sub>Si(2-Me-4(4*t*BuPh)Ind)<sub>2</sub>ZrCl<sub>2</sub>) was prepared according to WO 98/40331 (example 65).

#### **Organic porous support**

Polyethylene prepolymer was produced according to the procedure described in example 1 of WO 95/26369, under the following conditions: polymerisation temperature 0°C, AliBu<sub>3</sub> (AliBu<sub>3</sub>/ZN catalyst = 1 (w/w)), 1.5 bar-g of ethylene (conversion of 40 g<sub>PE</sub>/g<sub>cat</sub>). The support has a PBD of 0.285 g/ml, porosity 0.507 cc/g, and % of pores having diameter comprised between 0.1 µm (1000 Å) and 2 µm (20000 Å) of 76.19%.

#### **Preparation of the catalyst system**

4.6g of the support described above, were treated with H<sub>2</sub>O dispersed in hexane in order to deactivate the MgCl<sub>2</sub>/Ti-based catalyst, then dried in a flow of nitrogen. The support is contacted with 0.5mL of MAO solution (30%w in toluene) diluated with 1.5 ml of toluene to scavenge impurities and residual water.

The catalytic complex was prepared by adding 42mg of metallocene in 4.1ml of MAO solution (30% w/w in toluene).

The so obtained catalytic mixture is impregnated on support A (treated as described above) according to procedure described in WO 01/44319.

The obtained supported catalytic system contains 8.7 %w of Aluminium and 0.1% of Zirconium measured via Ion Coupled Plasma (Al/Zr = 294).

#### **Polymerization examples 1-3**

##### **General procedure**

Reactor cleaning: The autoclave is kept overnight under nitrogen flow, then 4 mMoles TEA (as 6 % w/v hexane solution) are added as scavenger, and 0.5 bar-g propylene are fed to prevent air from entering the reactor.

##### **step a)**

Propylene prepolymerization: 165 g propylene are fed at 40°C. The catalytic system is injected in the reactor as a dry powder (for prepolymer supported catalysts). Propylene is prepolymerised at 40°C for 10 minutes. At the end of this step the reactor temperature was

raised from 30 to 80°C in 10 minutes. At the same time, propylene is fed into the autoclave until 24 bar-g pressure are reached; for these two steps about 10-15 minutes are needed.

Propylene matrix polymerization: the PP matrix is polymerised in gas phase at 80°C and 24 bar-g pressure until 40 g propylene are consumed; then the autoclave is flashed to 0.1 bar-g propylene and the temperature is brought to 60°C.

Propylene intermediate washing: At 60 °C, 300 g propane are fed, under mild stirring, to remove the residual propylene monomer from the PP matrix from propylene residue for 10 minutes; this step is necessary because the presence of propylene traces in further ethylene/1-butene copolymerisation can give rise to an ethylene/propylene/1-butene terpolymer of lower molecular weight than desired; after cleaning, propane is vented off to 0.1 bar-g and T = 30 °C.

**step b)**

At 30 °C the ethylene/1-butene copolymerisation bath, as reported in table 1, is fed in the same autoclave in the presence of the polymer obtained in step a). At the same time the temperature is increased from 30 to 70 °C. The pressure is 21 bar-g or lower (as calculated from Aspen+ simulations). If required, H<sub>2</sub> is fed at this point in time.

When the desired temperature and pressure are reached, the copolymerization is run by continuously feeding ethylene and 1-butene at a defined ratio, until 500 g of monomers are fed.

After the gas phase copolymerisation has been completed, the reactor mixture is vented and cooled down to room temperature; The polymer is collected, dried, weighted for yield determination and further characterisation. Polymerization data and characterization of the polymers are reported in table 1.

table 1

Ex.	mg	t <sub>PP</sub>	t <sub>EBR</sub>	T <sub>p</sub>	ethylene (C <sub>2</sub> ) fed	1-but (C <sub>4</sub> ) fed	C <sub>2</sub> / (C <sub>2</sub> +C <sub>4</sub> )
		min.	min.	°C	g	g	molar
1	314	30	145	70	260	140	0.788177
2	260	15	113	70	412	138	0.856768
3	260	12	82	70	400	100	0.889065

table 1 (continued)

polytest	kgCOP/ g <sub>cat</sub> /h	IV	M <sub>w</sub> /M <sub>n</sub>	split (NMR)	X.S.	IV <sub>(XS)</sub>	C <sub>2</sub> <sup>*</sup>	C <sub>4</sub> <sup>*</sup>	T <sub>m</sub>	ΔH
		dl/g		%wt	% wt	dl/g	mol%	%mol	°C	J/g
1	0.5	1.33	2.4	81.2	69.2	1.27	78.2	21.8	150.5	11
2	1.1	1.74	2.8	87.9	79.8	1.99	79.1	20.9	151.9	10
3	1.4	2.10	3.2	84.7	66.4	n.a.	85.48	14.52	151.9	10

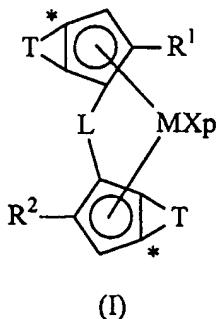
n.a. = not available

\* = content of ethylene and 1-butene in the copolymer obtained in step b)

note: no fouling in the reactor was observed and the polymer particles does not adhere to each other having a good flowability.

## Claims

1. A multistage process comprising the following steps:
  - a) polymerizing propylene and optionally one or more monomers selected from ethylene and alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$ , wherein  $\text{T}^1$  is a  $\text{C}_2\text{-C}_{20}$  alkyl radical in the presence of a catalysts system, supported on an inert carrier comprising:
    - i) one or more metallocene compound of formula (I):



(I)

wherein:

M is an atom of a transition metal selected from those belonging to group 3, 4, 5, 6 or to the lanthanide or actinide groups in the Periodic Table of the Elements;

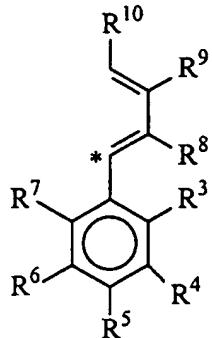
p is an integer from 0 to 3, being equal to the formal oxidation state of the metal M minus 2;

X, same or different, is a hydrogen atom, a halogen atom, or a R, OR,  $\text{OSO}_2\text{CF}_3$ , OCOR, SR,  $\text{NR}_2$  or  $\text{PR}_2$  group, wherein R is a linear or branched, saturated or unsaturated  $\text{C}_1\text{-C}_{20}$  alkyl,  $\text{C}_3\text{-C}_{20}$  cycloalkyl,  $\text{C}_6\text{-C}_{20}$  aryl,  $\text{C}_7\text{-C}_{20}$  alkylaryl or  $\text{C}_7\text{-C}_{20}$  arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X can optionally form a substituted or unsubstituted butadienyl radical or a OR' group wherein R' is a divalent radical selected from  $\text{C}_1\text{-C}_{20}$  alkylidene,  $\text{C}_6\text{-C}_{40}$  arylidene,  $\text{C}_7\text{-C}_{40}$  alkylarylidene and  $\text{C}_7\text{-C}_{40}$  arylalkylidene radicals;

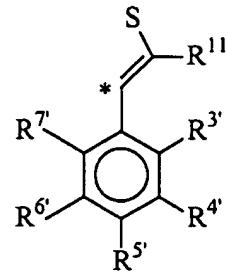
L is a divalent bridging group selected from  $\text{C}_1\text{-C}_{20}$  alkylidene,  $\text{C}_3\text{-C}_{20}$  cycloalkylidene,  $\text{C}_6\text{-C}_{20}$  arylidene,  $\text{C}_7\text{-C}_{20}$  alkylarylidene, or  $\text{C}_7\text{-C}_{20}$  arylalkylidene radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, and silylidene radical containing up to 5 silicon atoms;

$R^1$  and  $R^2$ , equal to or different from each other, are linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

$T$ , equal to or different from each other, is a moiety of formula (IIa) or (IIb):



(IIa)



(IIb)

wherein:

the atom marked with the symbol \* bonds the atom marked with the same symbol in the compound of formula (I);

$R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$ , equal to or different from each other, are hydrogen atoms or linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear  $C_1$ - $C_{20}$  alkyl substituents; with the proviso that at least one among  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  is a linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radical optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

$R^8$ ,  $R^9$  and  $R^{10}$ , equal to or different from each other, are hydrogen atoms or linear or branched, saturated or unsaturated  $C_1$ - $C_{20}$ -alkyl,  $C_3$ - $C_{20}$ -cycloalkyl,  $C_6$ - $C_{20}$ -aryl,  $C_7$ - $C_{20}$ -alkylaryl, or  $C_7$ - $C_{20}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more  $R^8$ ,  $R^9$  and  $R^{10}$  can join to form a 4-7

saturated or unsaturated membered rings, said ring can bear one or more C<sub>1</sub>-C<sub>10</sub> alkyl substituents;

R<sup>11</sup> is a hydrogen atom or a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>20</sub>-alkyl, C<sub>3</sub>-C<sub>20</sub>-cycloalkyl, C<sub>6</sub>-C<sub>20</sub>-aryl, C<sub>7</sub>-C<sub>20</sub>-alkylaryl, or C<sub>7</sub>-C<sub>20</sub>-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> equal to or different from each other, are hydrogen atoms or linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>40</sub>-alkyl, C<sub>3</sub>-C<sub>40</sub>-cycloalkyl, C<sub>6</sub>-C<sub>40</sub>-aryl, C<sub>7</sub>-C<sub>40</sub>-alkylaryl, or C<sub>7</sub>-C<sub>40</sub>-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two or more R<sup>3</sup> R<sup>4</sup> R<sup>5</sup> R<sup>6</sup> and R<sup>7</sup> can join to form a 4-7 saturated or unsaturated membered rings, said ring can bear C<sub>1</sub>-C<sub>10</sub> alkyl substituents;

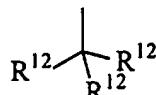
- ii) an alumoxane or a compound capable of forming an alkyl metallocene cation;
- b) contacting, under polymerization conditions, in a gas phase, ethylene with one or more alpha olefins of formula CH<sub>2</sub>=CHT<sup>1</sup>, wherein T<sup>1</sup> is a C<sub>2</sub>-C<sub>20</sub> alkyl radical, and optionally with a non-conjugated diene, in the presence of the polymer obtained in step a)

wherein the amount of the polymer obtained in step a) is higher than 4% and lower than 20% by weight of the polymer obtained in the whole process and the amount of polymer obtained in step b) is higher than 80% by weight and lower than 96% by weight of the polymer obtained in the whole process.

2. The process according to claim 1 wherein the catalyst system further comprises iii) an organo aluminum compound.
3. The process according to claims 1 or 2 wherein step b) is carried out in the presence of an additional organo aluminum compound.
4. The process according to anyone of claims 1-3 wherein in the compound of formula (I) M is titanium, zirconium or hafnium; p is 2; X is a hydrogen atom, a halogen atom or a R group wherein R is defined as in claim 1; L is selected from the group consisting of is Si(CH<sub>3</sub>)<sub>2</sub>, SiPh<sub>2</sub>, SiPhMe, SiMe(SiMe<sub>3</sub>), CH<sub>2</sub>, (CH<sub>2</sub>)<sub>2</sub>, (CH<sub>2</sub>)<sub>3</sub> and C(CH<sub>3</sub>)<sub>2</sub>; and R<sup>1</sup> and R<sup>2</sup> are methyl or ethyl radicals.
5. The process according to anyone of claims 1-4 wherein at least one among R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> is a linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>40</sub>-alkyl,

$C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radical, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.

6. The process according to anyone of claims 1-5 wherein  $R^5$  and  $R^{5'}$ , equal to or different from each other, are linear or branched, saturated or unsaturated  $C_1$ - $C_{40}$ -alkyl,  $C_3$ - $C_{40}$ -cycloalkyl,  $C_6$ - $C_{40}$ -aryl,  $C_7$ - $C_{40}$ -alkylaryl, or  $C_7$ - $C_{40}$ -arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements.
7. The process according to claim 6 wherein  $R^5$  and  $R^{5'}$ , equal to or different from each other, are branched  $C_1$ - $C_{40}$ -alkyl radicals.
8. The process according to claim 7 wherein  $R^5$  and  $R^{5'}$  are groups of formula (III):



(III)

wherein  $R^{12}$ , equal to or different from each other, is a  $C_1$ - $C_{10}$  alkyl radical.

9. The process according to anyone of claims 1 to 8 wherein in the compounds of formula (I)  $R^3$ ,  $R^4$ ,  $R^6$ ,  $R^7$ ,  $R^{3'}$ ,  $R^{4'}$ ,  $R^{6'}$  and  $R^{7'}$  are hydrogen atoms and  $R^{11}$  is a linear or branched, saturated  $C_1$ - $C_{20}$ -alkyl.
10. The process according to anyone of claims 1 to 9 wherein in the compound of formula (I) T are the same and they have formula (IIa) wherein  $R^9$  is a  $C_1$ - $C_{20}$  alkyl radical.
11. The process according to anyone of claims 1 to 9 wherein in the compound of formula (I) T are the same and they have formula (IIb).
12. The process according to anyone of claims 1 to 9 wherein in the compound of formula (I) T are the same and they have formula (IIa) wherein  $R^9$  is a hydrogen atom.
13. The process according to anyone of claims 1 to 9 wherein in the compound of formula (I) T are different and they have formulas (IIb) and (IIa).
14. The process according to anyone of claims 1 to 9 wherein in the compound of formula (I) T are the same and they have formula (IIIb), wherein  $R^{11}$  is a linear or branched, saturated  $C_1$ - $C_{20}$ -alkyl radical.
15. The process according to anyone of claims 1 to 14 wherein the inert carrier is a porous organic polymer.

16. The process according to anyone of claims 1 to 15 wherein step a) further comprises a prepolymerization step a-1) in which the catalyst system described in claim 1 is prepolymerized.
17. The process according to anyone of claims 1 to 16 wherein step a) is carried out in the presence of hydrogen.
18. The process according to anyone of claims 1 to 17 wherein step b) is carried out in the presence of hydrogen.
19. The process according to anyone of claims 1 to 18 wherein in step a) from 10% to 18% by weight of a propylene homopolymer or propylene copolymer containing up to 20% by mol of derived units of ethylene or one or more alpha olefins of formula  $\text{CH}_2=\text{CHT}^1$  is produced.
20. The process according to anyone of claims 1 to 19 wherein in step b) from 82% to 90% by weight of an ethylene copolymer having from 3% by mol to 60% by mol of derived units of comonomers of formula  $\text{CH}_2=\text{CHT}^1$  and optionally up to 20% of derived units of non conjugated diene, is produced.
21. The process according to anyone of claims 1 to 20 wherein in step a) a propylene homopolymer is produced.
22. The process according to anyone of claims 1 to 21 wherein in step b) an ethylene 1-butene copolymer having a 1-butene content ranging from 5% to 45% by mol is produced.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2004/008761

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08F297/08 C08F2/00 C08F4/643		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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X	EP 0 704 463 A (MITSUI PETROCHEMICAL IND) 3 April 1996 (1996-04-03) claims -----	1-18, 21, 22
A	US 2003/130443 A1 (RAUSCHENBERGER VOLKER ET AL) 10 July 2003 (2003-07-10) examples claims 4, 7 -----	1-22
A	US 5 280 074 A (SCHRECK MICHAEL ET AL) 18 January 1994 (1994-01-18) column 1, line 9 - line 15 column 2, line 1 - line 10 -----	1-22
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed		
*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *&* document member of the same patent family		
Date of the actual completion of the international search  27 October 2004		Date of mailing of the international search report  05/11/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer  Thomas, D

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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